



Screen-printed carbon electrodes modified with a bismuth film for stripping voltammetric analysis of platinum group metals in environmental samples



Bongiwe Silwana^{a,b}, Charlton van der Horst^{a,b}, Emmanuel Iwuoha^{a,1},
Vernon Somerset^{b,*,1}

^a SensorLab, Department of Chemistry, University of the Western Cape, Bellville, 7535, South Africa

^b Natural Resources and the Environment (NRE), Council for Scientific and Industrial Research (CSIR), Stellenbosch, 7600, South Africa

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ABSTRACT

The increasing use of platinum group metals, PGMs (e.g. platinum, palladium and rhodium) in catalytic converters and the increasing mining activities for these metals in South Africa, has increased the presence of these metals in the aquatic environment. For this reason, the developments of sensitive detection techniques for metal ions in environmental samples have been investigated in this study. The work reported in this paper describes the development of an adsorptive differential pulse stripping voltammetric procedure for the determination of palladium (Pd), platinum (Pt) and rhodium (Rh) in environmental samples collected from rivers in close proximity to mining activities in South Africa. A screen-printed carbon electrode coated with a bismuth film, SPCE/BiF was constructed. The optimisation of the experimental conditions performed, included an appropriate buffer solution for coating and the supporting electrolyte solution. The voltammetric procedure included pre-concentration of the metals using dimethylglyoxime (DMG) as chelating agent, followed by adsorptive differential pulse stripping voltammetry (AdDPSV) at appropriate deposition potentials for each of Pd, Pt and Rh. Other essential stripping voltammetric parameters optimised included the DMG concentration, composition of the supporting electrolyte, pH, deposition time, and deposition potential. Interference studies in the presence of Ni and Co have also been conducted and showed promising results. The results obtained for this investigation have shown that the detection limits of 0.008 $\mu\text{g/L}$, 0.006 $\mu\text{g/L}$ and 0.005 $\mu\text{g/L}$ were obtained for Pd(II), Pt(II) and Rh(III) determination respectively, using the SPCE/BiF sensor. The results obtained for Pd(II) determination of freshwater samples have shown that the concentration of Pd(II) in these samples ranged between 2.56–5.17 \pm 0.41 ppb ($n=3$). The results obtained for the Pt(II) concentrations ranged between 0.41–0.71 \pm 0.17 ppb ($n=3$). In the case of the Rh(III) determination, it was found to be 0.14–0.38 \pm 0.07 ppb ($n=3$). It was therefore concluded that the performance of the SPCE/BiF sensor was found to be more sensitive than the GCE/BiF sensor constructed in our laboratory in a previous study. It was further established that the SPCE/BiF sensor delivers more sensitive results in ammonia buffer (pH=9.2) solution, compared to acetate buffer (pH=4.8) solution.

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1. Introduction

In analytical chemistry, sensitivity and selectivity are some of the most important factors, particularly at low analyte concentrations and in the presence of interfering substances. High selectivity, even in trace analysis has been gained by progress in analytical instrumentation such as flame atomic absorption (FLAA) spectroscopy, inductively coupled plasma optical emission

spectroscopy (ICP-OES), inductive coupled plasma mass spectroscopy (ICP-MS) and neutron activation analysis (NAA). However, these sophisticated techniques are not suitable for *in situ* operation and the sensitivity of these methods is limited with the accompanying common metals and large excess of acids and inert salts interfering to some extent [1,2]. Furthermore, these techniques are also known to be time consuming and not suitable for field analysis of multiple samples [1–3].

Electrochemical techniques are among the very sensitive analytical methods available for the detection of toxic metal ions in environment samples, using stripping voltammetry as the analysis mode [4,5]. The classic instrument consists of a potentiostat/galvanostat with an electrochemical cell containing three

* Corresponding author.

E-mail addresses: vsomerset@csir.co.za, vsomerset@gmail.com (V. Somerset).

¹ ISE Members

electrodes (e.g. working, reference and auxiliary). However, the current trend in electro-analytical techniques is to miniaturize the whole instrument due to the many advantages of small devices including portability, low costs and less demand on service and operations, sufficient sensitivity and selectivity [6–8]. The combination of chemically modified electrodes with stripping methods can offer an excellent alternative for electrochemical analysis of metals at trace levels, increasing not only the sensitivity but also selectivity of the analysis. A common approach to increasing selectivity is to attach host molecules, which selectively interact with specific target molecules of interest [8–10].

As an alternative to toxic mercury, an environmental friendly use of bismuth and other metals have been investigated that is suitable for the determination of the metal ions in environmental samples. Various substrates (platinum, gold, glassy carbon, carbon paste, carbon fibre) for bismuth film formation are reported [10–13]. *In situ* or *ex situ* preparation of a BiFE including the effect of bismuth precursor salt used to prepare the film [13]. Bismuth was prepared by electrodeposition onto the micro disc electrode by applying an *in situ* electroplating procedure [14]. Screen-printed carbon electrodes (SPCEs) belong to the most suitable carbon electrodes for *in situ* environmental analysis [13–17]. Besides the electrodes, the potentiostat controlling the electrode system also has to be miniaturized, portable and easy-to-use. The coupling of disposable SPCEs with stripping techniques is more favourable in comparison with conventional stripping analysis, as the design and operation are greatly simplified, in accordance with the requirements of a decentralised assay [18–20]. Techniques for ink-modification and reagent-stabilization continue to improve, while more sophisticated methods for screen-printing and sensor-fabrication develop. Together with recent advances in microelectrode fabrication and array technology, it is surely only a question of time before low-cost commercial analytical instruments incorporating sensors/biosensors based on SPCEs become widely available, both for single- and multiple-analyte monitoring [21–25].

This study focussed on the determination of platinum group metals (PGMs) since it is of great concern as they are known to have some mutagenic and toxic effects, even at very low concentrations [10]. PGMs are known to have good catalytic properties and therefore their presence in the environment may trigger several chemical and biochemical processes, which may affect the environment negatively. The chemistry of platinum compounds in aqueous solutions is dominated by the formation complex compounds. Many of the salts of PGMs, particularly those with halogens or nitrogen donor ligands, are soluble in water that simplifies analysis [26–28].

Successful pre-concentration of trace metal ions present in complex media requires that the sorbent material meets a number of important criteria, including high selectivity for target metals, high loading capacity, fast sorption kinetics, excellent stability, and ability to be easily regenerated. Studies on PGMs have been reported using electrodes manufactured from a wide variety of materials. These studies have been previously reported on voltammetric behaviour at carbon paste and glassy carbon electrodes. However, for a number of reasons, such as preparation time, potential carry over problems or toxicity in the case of mercury electrodes, the use of the previously mentioned electrodes are continuously improved. Screen printing technologies has shown an attractive solution to this problem, allowing for the inexpensive mass production of such electrodes, and so allowing for the possible use of these electrodes as “one shot” disposable devices [29–31].

In our present study, we have used *ex situ* plating for the formation of the bismuth film electrode (BiFE), followed by firstly investigating the cyclic voltammetric behaviour of PGMs at our SPCE/BiF sensor in different buffer (both acidic and alkaline)

solutions. This was followed by optimising the experimental conditions necessary to quantify relatively low concentrations of PGMs in the presence of DMG as complexing agent, using adsorptive differential pulse stripping voltammetry (AdDPSV). The optimised method was then applied to the determination of the concentrations of Pd(II), Pt(II) and Rh(III) in environmental samples using our newly developed method. This study therefore reports the first application of a SPCE modified with a bismuth film (SPCE/BiFE sensor) for the analysis of Pd(II), Pt(II) and Rh(III) in environmental samples collected from the platinum mining area in South Africa.

2. Experimental

2.1. Chemicals and reagents

The standards for platinum (Pt), palladium (Pd) and rhodium (Rh) (1000 mg/L atomic absorption standard solution) and a standard Bi(III) solution (999 mg/L, AAS) and dimethylglyoxime (DMG) were provided by Fluka (Germany). All other reagents used were provided by Merck (South Africa) and included sodium acetate, ammonia (25%) ammonium chloride, hydrochloric acid (32%) and nitric acid (55%). Glacial acetic acid and ethanol (95%) were purchased from Kimix (South Africa). Alizarin Complexone was purchased from Merck, South Africa.

Precious group metal (PGM) stock solutions were prepared from 1000 mg/L, AAS standards solutions and standardised Bi(III) (100 mg/L) was used for the formation of the film on a SPCE. A stock solution of 0.01 M DMG was prepared by dissolution of the pure substance in absolute ethanol. Ammonium buffer solution was prepared from ammonium chloride and the pH was adjusted to the value of 9.2 with the addition of ultrapure ammonia (NH₃; 25%) and employed as supporting electrolyte solution. Acetic acid was used for pH control for the preparation of a sodium acetate buffer (pH=4.8) solution. Ultrapure water (Milli-Q plus; 18.2 MΩ; Millipore systems) was used in all experiments and standard solution preparations.

2.2. Apparatus

Voltammetric measurements were performed using a PalmSens® portable potentiostat/galvanostat, with the PS Trace program and accessories (PalmSens® Instruments BV, 3992 BZ Houten, The Netherlands), interfaced to a microcomputer controlled by PS 2.1 software for data acquisition and experimental control. The measurements were performed in a conventional electrochemical cell of 20.0 mL, employing the bismuth film modified carbon screen-printed electrode (SCPE/BiF) with 4 mm diameter provided by Dropsens (Oviedo, Spain) as working electrodes. A 3 M NaCl-type Ag/AgCl reference electrode, and a platinum wire auxiliary electrode, supplied by BASi (BASi Instruments, 2701 Kent Ave., West Lafayette, IN 47906, USA) was also employed. The measurement of pH values during the experiment performed by means of a microprocessor pH meter with custom buffers (the model HI 221 series, Hanna, instruments). All experiments were performed at room temperatures [12].

2.3. Preparation of bismuth film electrode

The screen-printed carbon electrode (SPCE) was connected to the potentiostat as working electrode using a 1 meter length cable provided by the electrode manufacturer (PalmSens®). A conventional three-electrode system was employed consisting of a single connector screen-printed working electrode, Ag/AgCl reference electrode, and a platinum wire auxiliary electrode. High purity argon gas was used to displace oxygen from the electrochemical cell before results were collected [11]. The three electrode system

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